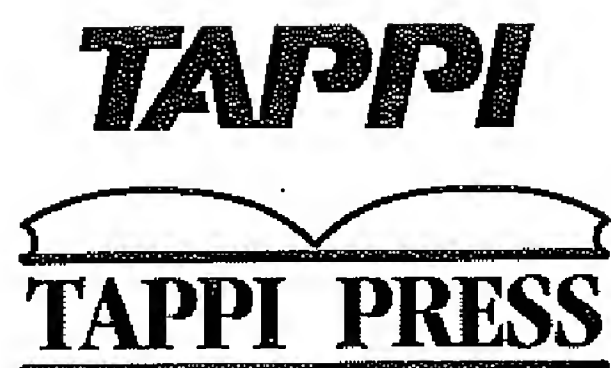


William E. Scott, Ph.D.



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Chap

Introdu Wet En

A recent review can paper in million on paper impressive for the nonfibrous furnish. Broz additives and objectives:

- Achievement
- Enhancement

The first object specific importance indication of further category is more productivity processing a

1. Wet end proper

Every paper specification and manufacturer inherent properties enables the these deficiencies needs more

a. Category influen

Most paper end chemist the following

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- Mechanical ing resista ing endur face stren
- Appearance opacity, g
- Barrier ar
- Permanent version, c

The follow

c. Mechanical properties

Mechanical properties (strength properties) are functions of bond strength, fiber strength, and sheet formation. If formation is allowed to degrade beyond a certain extent, then strength properties are adversely affected. This is a second order effect, however, compared to the influence that wet end chemistry has on bond strength. Specifically, fiber-fiber hydrogen bonding can be greatly enhanced by the use of dry strength additives such as starch. The use of such additives has been common for decades and will become more important in the future as the recycled fiber content of furnishes increases. Consequently, the papermaker must understand the factors that affect starch retention and set up system conditions accordingly. Other chemical additives, such as fillers and sizing agents, interfere with fiber-fiber bonding and reduce paper strength.

It is also commonly experienced that neutral and alkaline papermaking conditions promote improved fiber-fiber bonding relative to acid papermaking. Many companies have converted from acid to alkaline papermaking during the past decade.

Many paper grades have to retain a high level of strength when saturated with water. In other words, they must have "wet strength." Paper has no inherent wet strength due to the nature of fiber-fiber bonds. Hence, wet strength must be achieved through the use of additives. Such additives, called wet strength resins, are widely used in the paper industry. They are cationic, polymeric materials that are added to the furnish prior to sheet formation, and must be retained and cured in the paper web.

d. Appearance properties

Dyes and mineral pigments (fillers, optical brighteners, colored pigments) are a principal means of influencing the appearance of paper, as described by the properties color, opacity and brightness. Chemical additives have less effect on gloss. These materials either scatter light more effectively than fibers or selectively absorb specific visible light wavelengths. Dyes interact specifically with visible light and this reaction is affected by a wide range of chemical and physical factors. Hence, the papermaker must closely control the chemical environment and physical conditions of a furnish in order to avoid color changes. It is also important that conditions be established that will promote the ion exchange retention mechanism of dyes.

In order to attain high opacity and brightness, it is necessary to retain high levels of mineral filler pigments in the formed web. Mineral

pigment light scattering efficiency is also a strong, inverse function of pigment aggregation. These two factors pose a dilemma to the papermaker since the flocculation chemistry that promotes filler retention also promotes filler aggregation. Good understanding of the interactions that occur among fillers, fiber and retention aids is imperative in order to achieve the required balance.

e. Barrier and resistance properties

One of the major weaknesses of paper is that wood fibers have absolutely no natural resistance to water penetration. Hence, when this property is required (as it is for most paper grades), it must be achieved either by adding a sizing agent prior to sheet formation or treating the formed paper with a water-resistant coating or saturant. The former practice falls into the realm of wet end chemistry.

Internal sizing (wet end sizing) entails retention of either an alum-rosin sizing agent or a synthetic sizing agent in the paper web when it is formed. The sizing agent is mixed with the fibers and other ingredients prior to the paper machine headbox. This agent, which imparts hydrophobic character to the fiber surfaces, must be retained rapidly and to a high degree in order to be effective and avoid machine cleanliness and runnability problems. The effectiveness of sizing agents is influenced by a number of furnish and machine factors.

f. Permanence

Traditionally, permanence has been of interest primarily to librarians and archivists. While still important to these groups, others have become aware of the problem of paper aging and the matter is receiving increased attention.

Chemistry plays a large role in paper permanence. Indeed, it is well-established that alkaline paper is far more permanent than acid paper, under practically all circumstances. It is also recognized that the chemical and physical condition of fibers, impurities remaining in poorly washed pulps, heavy metal ions, and calcium carbonate fillers also play roles in determining paper permanence. These all fall into the category of wet end chemistry. Thus, much of the work being done to increase permanence has focused on improvements in wet end chemistry and wet end chemistry control.

g. Closing comments

The above discussion, while abbreviated, nevertheless illustrates the central role played by wet end chemistry in the attainment of the paper property values required by grade specific-

Introduction

cations. This ten in the ch

2. Wet end machinery (runnability)

Wet end chemistry has a number of roles in papermaking. On one hand, it can enhance drainage, reduce foam, keep solids levels down. Conversely, it can cause deposits, scaling, machine inefficiencies. So situations are

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Drainage is influenced by fines-fines fill and porous, ciously and r and tight, the and enhance tem determin for in the dr

b. Deposits

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c. Foam and

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Chapter 9

Wet Strength Additives

1. Introduction

In this chapter, we will introduce the most important aspects of wet strength chemistry. Some excellent comprehensive reviews of wet strength have been published recently (See References [1-5]). Reference [2] contains a particularly extensive literature survey.

Wet strength additives, like dry strength additives, are polymeric materials that must be adsorbed by furnish components in order to be effective. In addition, all common wet strength resins must also undergo a curing step before they impart wet strength to paper. Thus, we add another layer of complexity in wet end chemistry interactions.

Paper is formed by filtering and thickening fibers and other particles from a water slurry and pressing and drying the formed web. When the sheet is consolidated in the press section, a few bonds form between fibers. However, the majority of the interfiber bonding occurs when the water is removed in the dryer section and surface tension forces bring the fibers into very close contact with one another.

Since hydrogen bonding plays a central role in interfiber bonding, and water molecules are capable of participating in extensive hydrogen bonding interactions, it is not surprising that paper loses most of its strength when it is brought into contact with water and fiber-fiber bonds are replaced by fiber-water bonds. Non-wet strength paper typically retains only 2-10% of its original dry strength when saturated with water. This property is a liability for a number of paper uses.

It is estimated that 5-10% of all paper and paperboard is given wet strength when it is manufactured. **Table 9-1** lists a number of paper grades that require some degree of paper strength in the presence of water.

2. Definition of wet strength paper

It is possible to produce papers that will retain more than 50% of their dry strength when saturated with water. Most wet strength grades will fall into the 20-40% category, however, and there is some general agreement that paper whose wet tensile strength is more than 15% of its dry

tensile strength should be considered to be wet strength paper. (Wet strength is often expressed as the "wet-to-dry" ratio of a strength property. Tensile strength is a common strength property used for this purpose.)

Wet strength papers are also classified in terms of their wet strength permanence. Non-wet strength paper loses its strength within seconds of being saturated with water. Some wet strength treatments will only slow down this strength loss and such papers are said to have "temporary" wet strength. Other additives give "permanent" wet strength in that under normal use conditions their wet strength properties remain intact indefinitely.

Table 9-1. Typical grades of paper that require wet strength

- Paper towels and other absorbent wipes
- Wrapping and bag papers, sack papers, carrier bags
- Folding boxboard carrier stock
- Photographic paper, filter paper
- Milk carton raw stock
- Map papers
- Currency papers

3. Wet strength mechanisms

Dunlop-Jones points out that in order for paper to retain its strength when wet, it is necessary to take one or more of the following actions:^[2]

- Add to, or strengthen, existing bonds
- Protect existing bonds
- Form bonds that are insensitive to water
- Produce a network of material that intermingles with fibers

Wet strength additives are believed to achieve the above phenomena by the following mechanisms.

Create a cross linked network within and around fibers that inhibits swelling and water sorption and protects existing interfiber hydrogen bonds. This mechanism is sometimes referred to as a *bomo-cross linking* mechanism.

Create new, water resistant, interfiber bonds (covalent, acetal, hydrogen bonds) that cross-link fibers. This mechanism has been called the *reinforcement, new bond, or co-cross linking* mechanism. (Note that the two mechanisms are not mutually exclusive.)

4. The need for curing wet strength additives

In Chapter 8 we discussed dry strength additives and pointed out that it was critical that they be retained on fibers with high efficiency.

If this is accomplished, then it can be expected that a good strength response will follow. This is not necessarily the case with many wet strength resins, where it is possible to have high retention and poor wet strength performance.

The reason for this is that most wet strength resins require a curing stage before they become effective. Even though curing does not occur in the paper machine wet end, curing is influenced strongly by the chemical characteristics of the sheet and, because of this, curing can be considered to be a wet end chemistry matter. We will address this matter below with reference to each common wet strength resin.

5. Wet strength resins

The earliest approaches to wet strengthening paper involved heating it to high temperatures or parchmentizing it in dilute sulfuric acid. Later, in the 1930s, it was discovered that certain water-soluble synthetic resins could impart wet strength to paper when added to the furnish and cured on the paper machine. Since that time, there has been a rapid growth in the use of wet strength resins and now more than \$100 million worth of these materials are used every year by the US paper industry.

To be an effective wet strength resin, a material must have the following four properties:

- It must be polymeric and provide mechanical strength to protect fiber-fiber bonds against swelling and disruption.
- It must be cationic and provide the attraction to negative cellulose fibers needed for rapid and complete retention.
- It must be water-soluble or water-dispersible to insure uniform distribution throughout the furnish.
- It must be chemical network-forming (usually thermosetting) and provide paper with resistance against swelling by water.

While many different substances have been used as wet strength resins, the four materials listed in Table 9-2 have found the most applications.

Table 9-2. Most commonly used wet strength resins

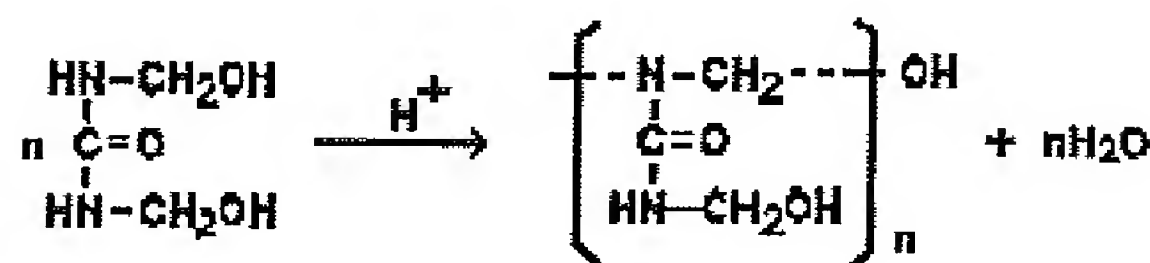
- Urea-Formaldehyde (UF)
- Melamine-Formaldehyde (MF)
- Polyamide-Epichlorohydrin (PAE)
- Polyamine-Epichlorohydrin

6. Urea-Formaldehyde Resin

a. Chemical structure

The first wet strength resins evolved from an early practice of impregnating paper with formaldehyde. Developments included the reaction

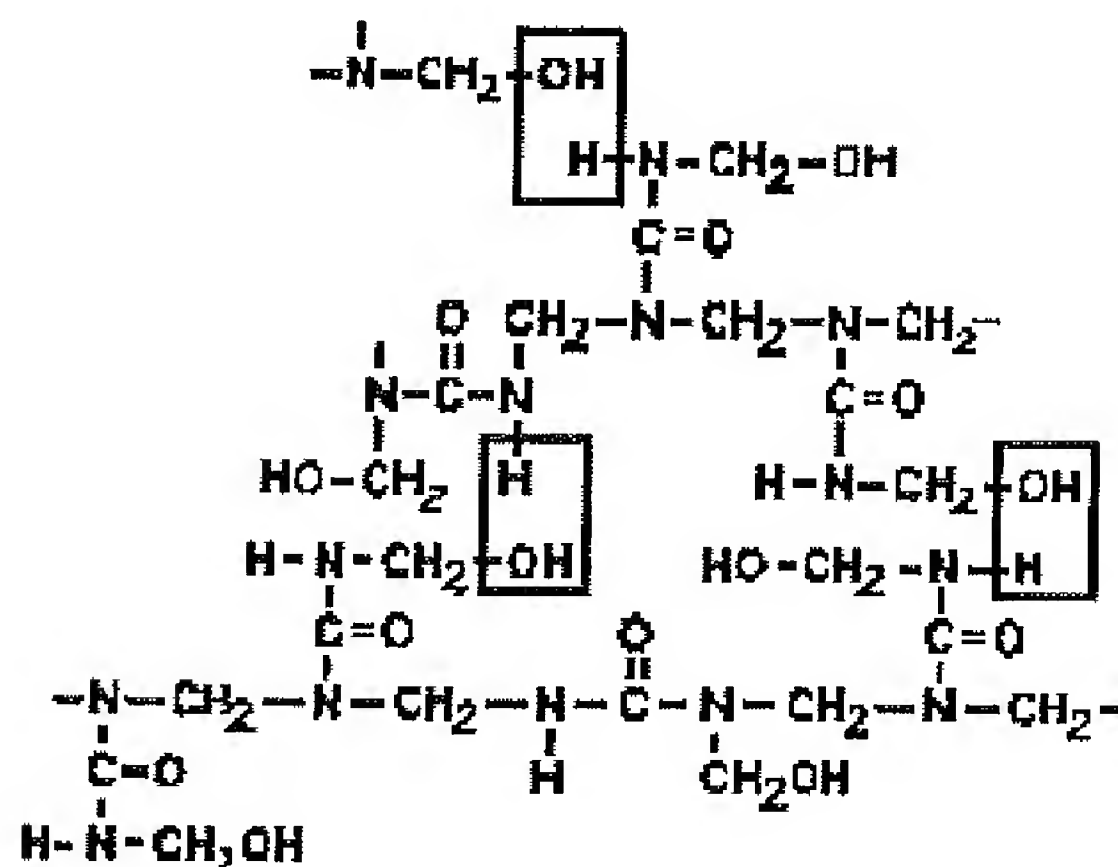
of urea with formaldehyde to produce dimethylolurea (Fig. 9-1), which did impart wet strength, but whose low solubility made it impractical for wet end addition.



Cross-Linking of Dimethylolurea

Figure 9-1. Reaction of urea and formaldehyde to produce dimethylolurea

Further research concentrated on producing a polymeric material. The primary reactions involved are illustrated in Fig. 9-2. The resin was still not soluble and this problem had to be overcome before urea-formaldehyde resins (UF resins) became viable wet strength additives.



Cross-Linking of Dimethylolurea
(Boxes indicate where water may split out)

Figure 9-2. Cross-linking of dimethylolurea to form a resin that imparts wet strength to paper

A water-soluble, anionic material was next produced by incorporating sodium bisulfite or glycine in the product. This resin could be precipitated onto fibers by alum. Finally, it was discovered that incorporation of diethylene-triamine or other polyfunctional amine in the resin structure would produce a cationic polymer that was naturally attracted to pulp fibers and retained well.

UF resins are delivered to the mill as 25-35% solutions that have been polymerized to a small degree. They continue to polymerize on standing and must be used before they lose their effectiveness due to overpolymerization.

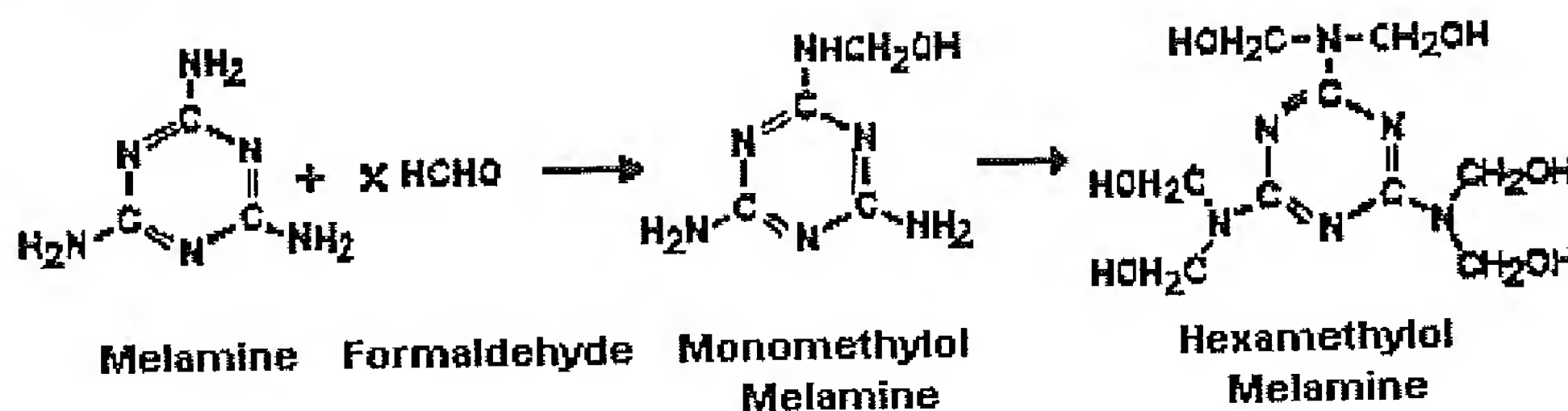


Figure 9-3. The reaction of melamine with formaldehyde to produce methylol melamines, the first step in the production of MF wet strength resin. Trimethylol melamines were found to be most effective.

b. Use of UF resins in the paper mill ^[3]

UF resins should be filtered and diluted to about one percent solids prior to addition. Since they are acid curing, alum or some other acidic material must be present. The headbox pH of a machine using UF resins must be between 4.0-4.5 and the pH of the produced paper must be in the same range.

Urea-formaldehyde resins are used in amounts of 0.5-3.0 percent, dry basis, depending on the wet strength requirements of the paper being made. It is usually added at the fan pump. When rosin size is used, it is essential that the aluminosize reaction occur first, before the cationic UF resin has an opportunity to react with rosin to produce a foamy complex and deposits.

UF wet strength paper does not usually reach its final cured state on the paper machine and it must receive an accelerated cure (5-15 minutes at 104°C) prior to testing. It is important that a test specimen be completely saturated with water. This may require an extended soaking time or the use of a wetting agent if the paper is sized.

Fresh UF wet strength broke can be repulped without difficulty. Fully cured UF resin must be treated at pH 3-4 at 65°C or higher under repulping conditions in order to break down the resin.

Concentrated UF resin is highly cationic and will react strongly with any anionic material that it contacts. Dilute resin can tolerate mildly anionic materials but will react with strongly anionic materials. Both concentrated and dilute solutions polymerize rapidly at pH values much below 6.0.

Due to the health hazards associated with free formaldehyde, the use of UF resins by the paper industry has been much reduced in recent years. Whenever they are used, strict adherence to rigorous safety standards is mandatory.

7. Melamine-formaldehyde resin ^[2,3]

a. Chemical structure

The second resin patented for use in the paper industry was melamine-formaldehyde (MF),

which was first used in the early 1940s. The first step in the preparation of MF resin is the reaction of formaldehyde with melamine to produce methylol melamines (Fig. 9-3). Trimethylol melamine was found to be the most effective product which, when treated with hydrochloric acid, produces a highly cationic colloidal suspension that is very substantive to papermaking fibers. Commercial preparations containing a range of formaldehyde-to-melamine ratios are available.

Several reactions are possible, but it is believed that the formation of ether and methylene cross-links are important in the development of wet strength (Fig. 9-4). High temperature and low pH promote cross-linking reactions.

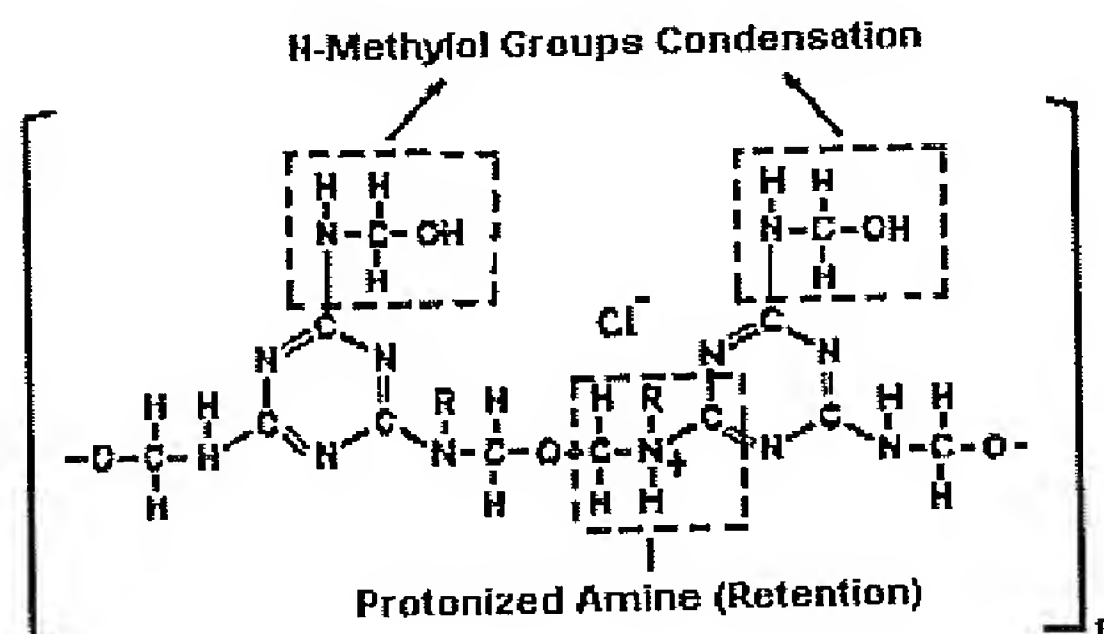


Figure 9-4. Potential cross-linking sites on the melamine-formaldehyde colloid. Ether and methylene linkages are thought to be important in wet strength development.

b. Use of MF resins in the paper mill ^[3]

MF resins are delivered to the mill in two forms, a dry powder or a ready-to-use acid colloid form. The powder must be dissolved in dilute acid and aged under specific conditions before use. Both forms take on a strong cationic charge under acid conditions. MF resin makedown and handling details are described in Reference [3].

MF resin addition levels vary from less than 1 percent, based on dry fiber weight (e.g. toweling), to 5 percent (very high wet strength papers). For most grades, 1-3 percent provides satisfactory results.

MF resins should be added as close to the headbox as possible (one percent resin solution), while still allowing time for uniform distribution and adsorption. Avoid subjecting the material to refiners and Jordans. Optimum addition points vary widely from mill to mill.

When properly used, other additives such as sizing agents, alum, and starch do not interfere with MF resins. However, when incorrect addition sequences or addition point placements are employed, reactions can occur between MF resin and rosin or starch that result in machine deposits and spots in paper.

Stock pH plays a particularly crucial role in the resin cure attained on the paper machine. Within the normal papermaking pH range of 4.5-5.3, MF resin cures rapidly and should give adequate wet strength after normal drying on the paper machine. Machine pH's in the 5-6 range may result in incomplete cure. This may be checked by heating samples in an oven at about 120°C for 10 minutes and checking for wet strength improvement. If improvement is noted, then one should expect additional cure to occur as the paper is stored.

High sulfate levels in the stock (> 200 ppm) have been found to be detrimental to MF resin efficiency, although a small amount of sulfate (25-100 ppm) has been found to be beneficial.

MF resin treated paper should be repulped directly off the paper machine, whenever possible, since it is often not fully cured. High tem-

perature (75-90°C) and low pH (2-3% alum) give the best results.

8. Neutral or alkaline curing polyamide wet strength resins

a. Chemical structures [1,2,5]

Approximately thirty years ago, wet strength polyamide (PAE) resins that could be used under neutral or alkaline papermaking conditions were invented. These materials are now the most common wet strength additive. A multi-step synthesis sequence was followed, similar to that for the production of nylon. In the first step (Fig. 9-5) a dibasic acid is reacted with a triamine to give a polyamide.

Next, the polyamide is treated with epichlorohydrin to alkylate secondary amine groups and produce tertiary aminochlorohydrin groups (Fig. 9-6). These groups self-alkylate to form 3-hydroxyazetidinium groups, which are responsible for the cationic character and reactivity of the wet strength resin. The resultant product consists of a relatively low molecular weight, cationic polyamide (<100,000) having many reactive side groups.

PAE resins are believed to undergo at least two kinds of reactions that contribute to wet strength. One reaction involves the reaction of an azetidinium group in one molecule with a secondary amine group in another molecule, to produce a cross-link between the two molecules.

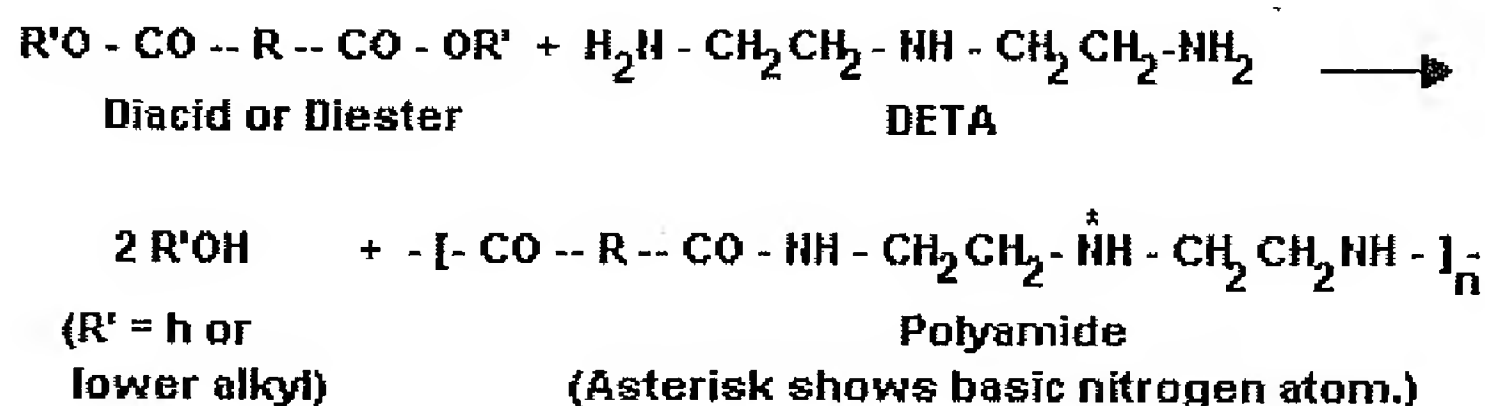


Figure 9-5. Preparation of polyamide-epichlorohydrin (PAE) wet strength resins. Step one: the synthesis of a polyamide from a dibasic acid and a triamine.

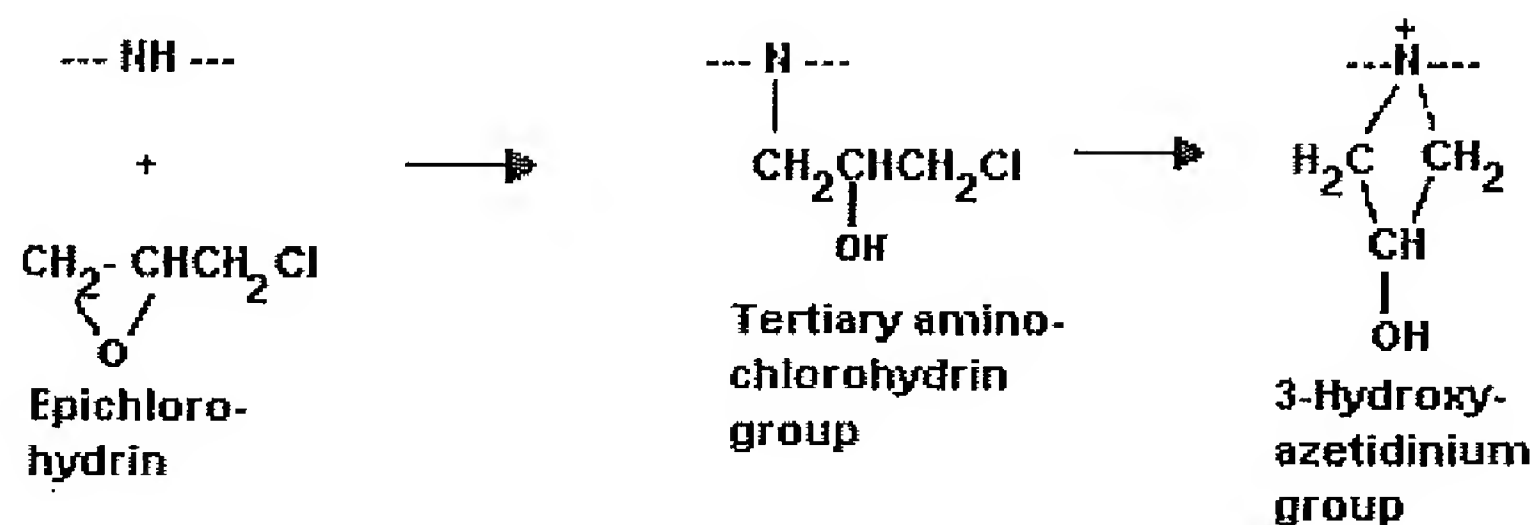


Figure 9-6. Preparation of polyamide-epichlorohydrin (PAE) wet strength resins. Step two: alkylation of the secondary amine groups in the polyamide produced in synthesis step one to produce tertiary aminochlorohydrin groups, which self-alkylate to form 3-hydroxyazetidinium groups which are responsible for the reactivity and cationic character of this wet strength resin.

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In the second reaction, at least two azetidinium groups on a single resin molecule react with carboxyl groups on two different fibers to produce an interfiber cross-link.

b Use of polyamide epichlorohydrin resins in papermaking^[3]

For stability purposes, PAE resins are acidified to a pH of 3.5-6 at the end of their preparation. Therefore, acid resistant pipes, pumps, and tanks must be employed. The resins are shipped at solids contents in the 12.5% to 33% range and can be handled by a variety of pumps. PAE resins are thermosetting, which means that they will polymerize to a water-insoluble condition by the action of heat alone. It is suggested that storage tank temperatures be kept below 30°C.

PAE resins can be used in headbox pH ranges of 5-9, however, the preferred range is 6-8. At lower pH's the reactivity of the resin is reduced. Typical PAE addition levels are 0.25% to 0.75%. They are often added at the fan pump, or earlier in the system if longer retention times are desired.

At the 25%-33% solids levels the resins are approaching their solubility limits, and will precipitate when mixed with practically any other substance. In addition, since they are highly cationic, PAE resins are incompatible with practically all types of anionic materials. Raising the pH above the normal storage value will accelerate the self cross-linking reactions and cause the resin solution to gel.

Dilute PAE solutions are compatible with some mildly anionic materials, but incompatible with strong anionics. Thus, it is important to keep PAE addition points on the paper machine well separated from anionic additive addition points. Rosin size is a good example. Rosin and PAE resins react to form foamy complexes and deposits. Raising the pH above 5 will gel dilute resin solutions.

PAE resins do not normally come to full cure on the paper machine and further polymerization occurs in the hot paper roll. Consequently, in order to predict the final level of wet strength that will be achieved, it is common practice to oven cure paper samples at 80°C for 30 minutes prior to testing.

Freshly made PAE wet strength paper can be readily repulped because it is not fully cured. Fully cured paper must be treated with more severe conditions. At the minimum, hot (>80°C) alkaline conditions (pH 11) are needed. In certain cases, it is necessary to employ an oxidizing agent, such as sodium hypochlorite, to break down the wet strength bonds.

9. Factors affecting the performance of wet strength resins

As with other cationic polymeric additives, many factors influence wet strength resin effectiveness. Fig. 9-7 illustrates the four areas of interest: the resin, the fibers, the chemical

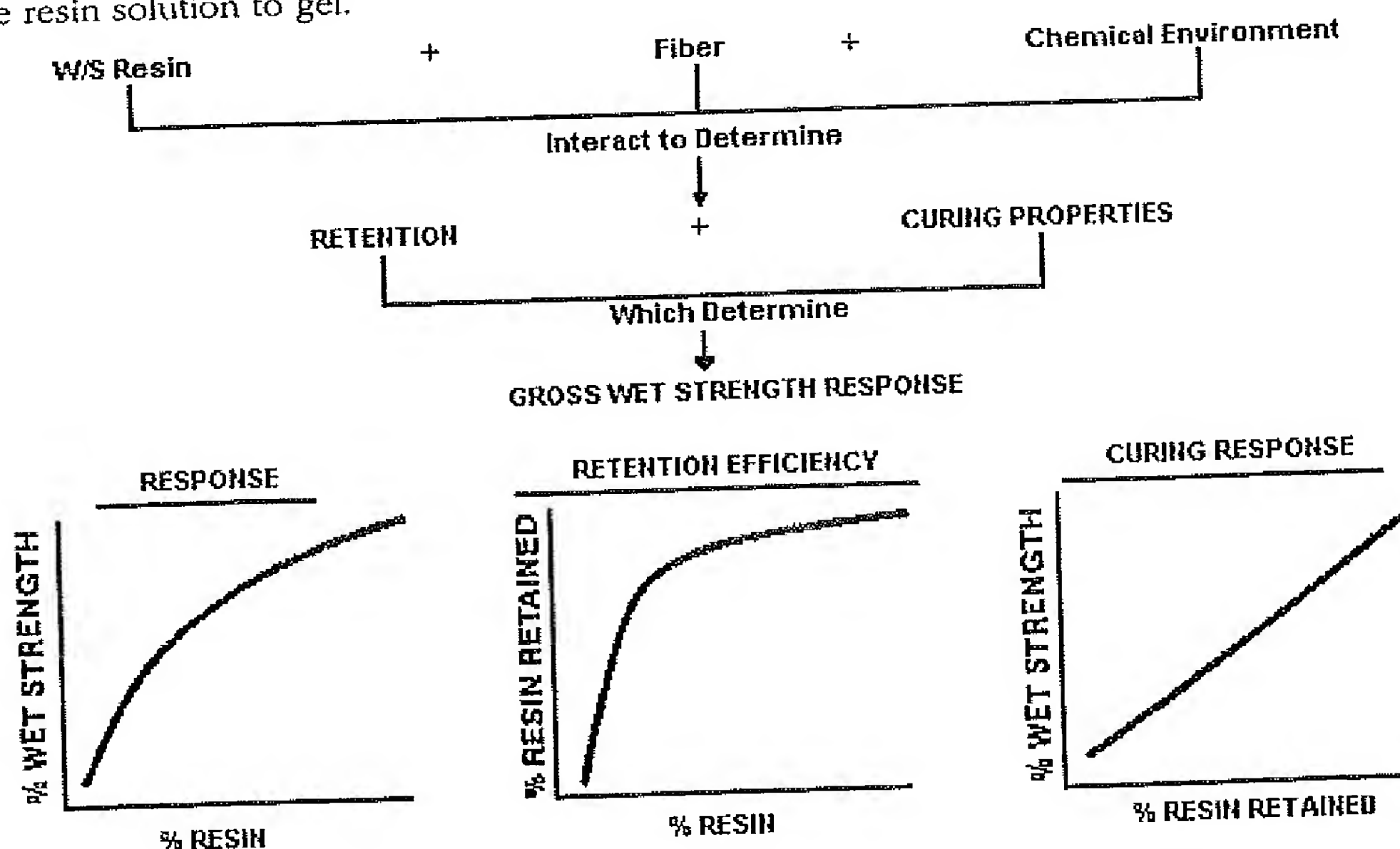


Figure 9-7. The four factors — resin, fiber, chemical environment, and machine conditions — that influence resin retention and curing and, in turn, produce wet strength.

environment, and the machine conditions. These interact to produce resin retention and curing which, in turn, produce the level of wet strength achieved.

Note that unlike other polymeric cationic additives, a high retention rate is insufficient to insure effective performance. The retained polymer must also be cured before a wet strength response is obtained.

10. Factors affecting the adsorption of wet strength resins by pulp fibers

Table 9-3 lists a number of important variables that influence resin retention by papermaking fibers.

Table 9-3. Variables important to the retention of wet strength resins by papermaking fibers⁽⁵⁾

- Fiber anionic sites
- Pulp consistency
- Contact time
- Resin concentration
- Pulp refining

a. Pulp carboxyl content

The carboxyl content of pulps affects resin performance because ionized carboxyl groups provide anionic adsorption sites for resin molecules. The higher the carboxyl group content, the more rapidly and more extensively will a pulp retain resin molecules. In general, unbleached softwood kraft pulps have the highest carboxyl contents, followed by bleached hardwood kraft and bleached softwood kraft, and finally, bleached softwood sulfite pulp. Wet strength resin retention follows the same order.

Wet strength resins exhibit typical Langmuir adsorption behavior, with the first resin added being completely adsorbed. As increasing amounts of resin are added, adsorption continues, but at a decreasing rate, due to impending saturation of the fiber anionic sites. The path of wet strength development parallels the adsorption behavior for the most part, with the initial resin having the most effect.

b. Pulp consistency and contact time

Both pulp consistency and contact time affect resin retention. The adsorption process is more rapid and complete at higher consistencies. This is presumably because at higher consistencies the polymer molecules have shorter distances to travel before colliding with a fiber surface than at lower consistencies. The data in Table 9-4 supports this point.

Table 9-4. Effect of pulp consistency and contact time on resin retention⁽⁵⁾

Pulp Consistency	Contact Time	Resin Retained, Percent of Furnish	Tensile, Percent Wet/Dry
2.5%	20 sec	70	28
	5 sec	67	26
0.25%	20 sec	47	24
	5 sec	47	23
0.02%	20 sec	34	23
	5 sec	27	20

c. Resin dilution

To gain the best resin distribution, it is imperative that it be diluted at least 10:1 with fresh water. Fresh water is preferred because white water and other kinds of dilution water may contain anionic substances that will react with the resin and neutralize it.

d. Pulp refining

Refining significantly enhances the performance of PAE resins only at high resin addition levels because at high resin levels, a more highly refined stock will have greater surface area available for resin adsorption (i.e. higher resin capacity). At low resin levels, even lightly refined fibers will have sufficient surface area to adsorb all of added resin and no noticeable effect of refining on wet strength will be found.

11. Effect of the chemical environment on resin performance

In addition to the resin retention factors discussed above, the chemical environment plays a key role in determining wet strength resin performance (Table 9-5).

Table 9-5. Chemical environment variables that affect wet strength development

- Chlorine residuals
- pH
- Stock temperature
- Anionic contaminants

a. Effect of chlorine residuals on PAE resin performance

As was mentioned earlier, sodium hypochlorite is used often to break down PAE resin during broke reworking. Active chlorine present in papermaking stock (from repulpers or bleach plant carryover) will also react with PAE resin and reduce its effectiveness. Fig. 9-8 illustrates this point. In such instances, the stock should be treated with an antichlor, such as sodium sulfite, prior to resin addition.

Wet Tensile
(lb/in; 2 wks
natural aging)

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b. pH

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Wet Strength Additives

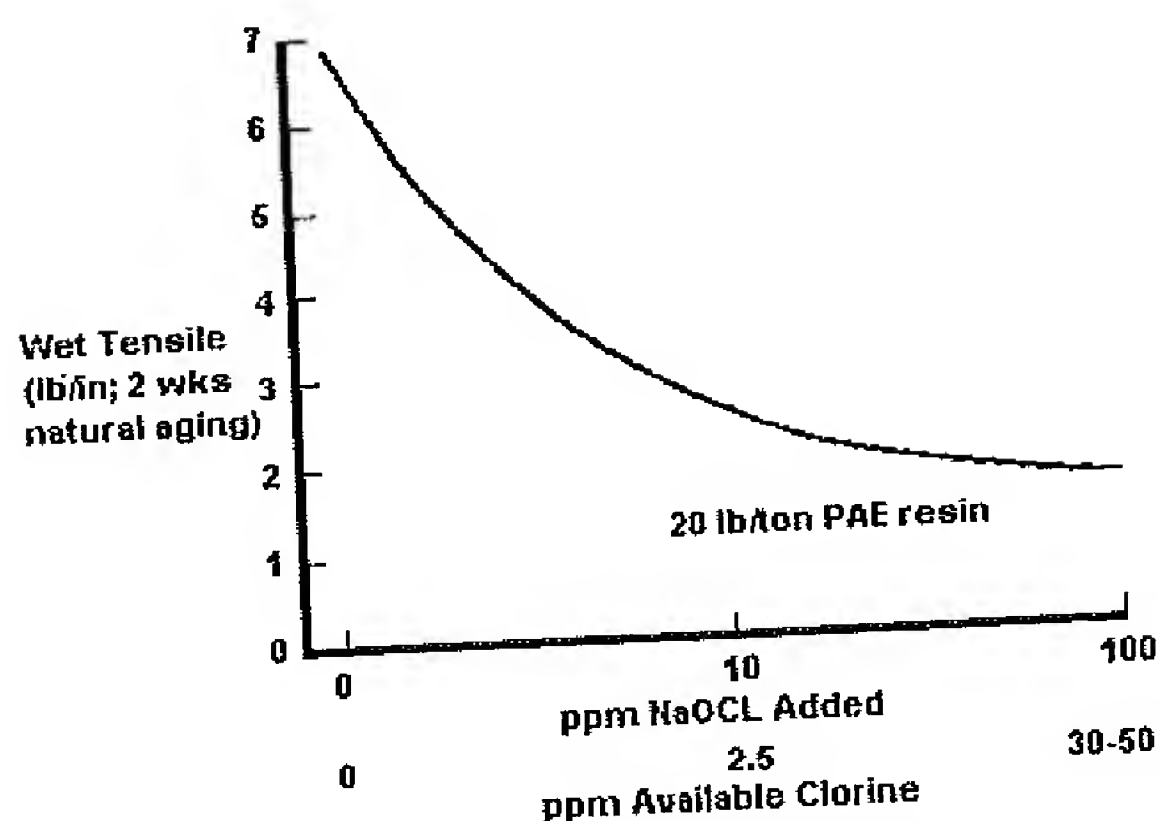


Figure 9-8. Effect of residual chlorine on wet strength

b. pH

PAE resins are effective over a pH range of 5-9. Below pH 5, resin effectiveness declines considerably for two reasons. First, pulp carboxyls are less ionized at low pH levels and become less attractive for the cationic resin. Second, at low pH levels, the secondary amine groups on the resin molecule become protonated and do not react readily in cross-linking reactions with azetidinium groups. Fig. 9-9 illustrates the effect of pH on PAE resin performance.

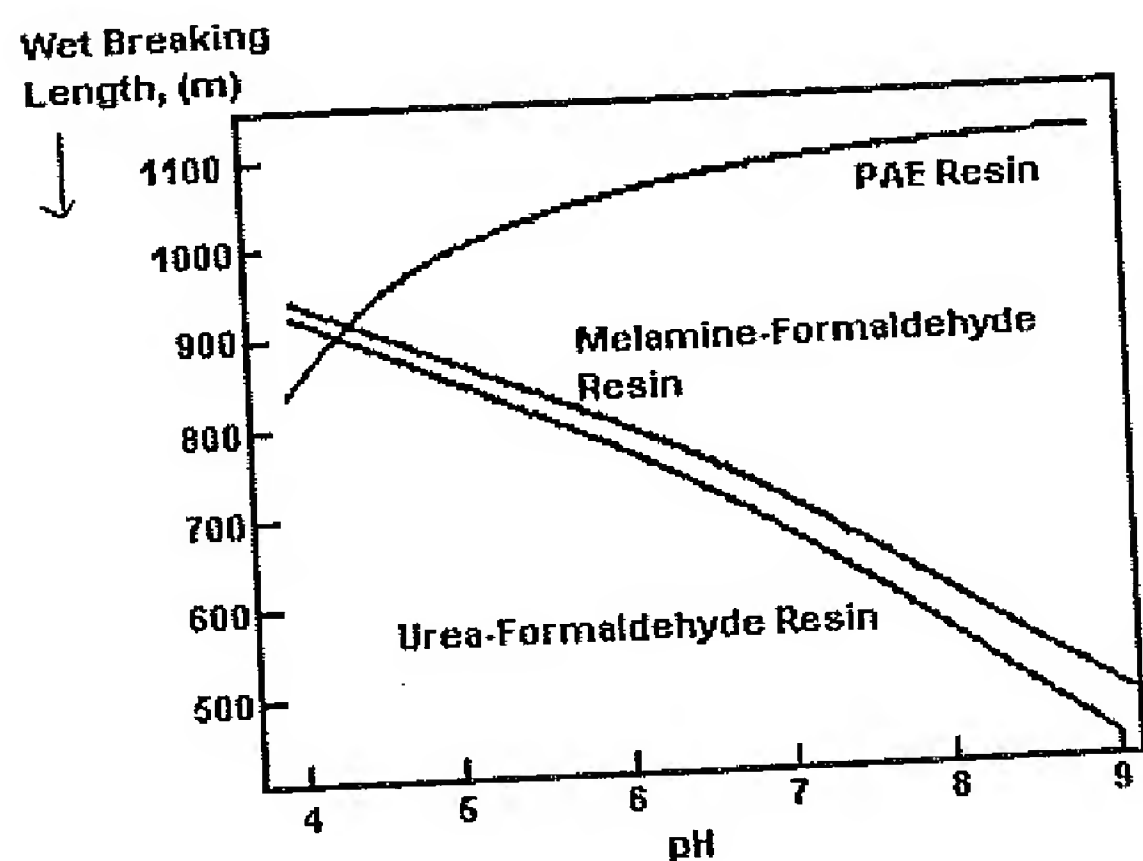


Figure 9-9. Effect of pH on wet strength development

UF and MF resins require acid pH values in order for wet strength to be developed by curing. If the sheet extracted pH is greater than about 4.5, then curing will be adversely affected.

c. Stock temperature and PAE performance

Prolonged exposure to high stock temperatures tends to reduce PAE resin efficiency. This may be due to the hydrolysis of azetidinium groups. This is a relatively slow reaction, but the resin should not be kept in contact with high temperature stock for long periods of time.

d. Interfering substances

Interfering substances such as lignin compounds, hemicelluloses, pulp mill carryover, bleach plant carryover, recycled papermaking additives, and anionic dispersants can react with cationic wet strength resins and interfere with their adsorption on fibers. Thorough washing or treatment of stock with a charge neutralizing substance (e.g. alum) prior to resin addition is necessary when high levels of interfering substances are present.

Sometimes cationic resins will precipitate small quantities of "color bodies" onto fibers and cause brightness reversion in the produced paper. This is usually a reaction between the cationic resin and an anionic color body. A similar reaction occurs between resin and anionic dyes. This can be a particularly serious problem in the manufacture of deep shade wet strength papers.

There is at least one instance where the reaction between cationic PAE and anionic polymers can be put to good use to enhance resin retention by fibers having low carboxyl content. In this case, anionic carboxymethyl cellulose (CMC) is reacted with PAE to form a weakly cationic complex (called a "symplex") that adsorbs onto the fiber surfaces. In essence, the CMC provides the carboxyl groups required to attract more PAE onto the fiber surface. Fig. 9-10 illustrates the effect of adding CMC to PAE in a handsheet study.

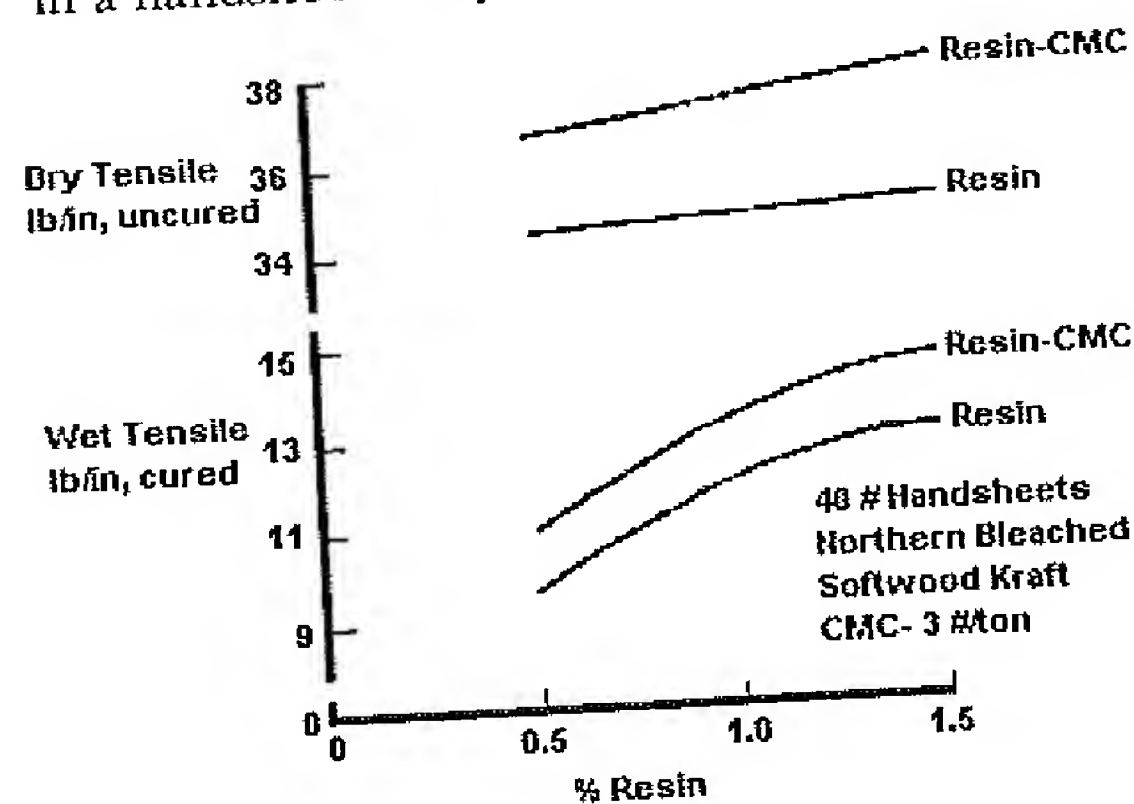


Figure 9-10. Effect of adding CMC to PAE in the preparation of wet strength paper

12. Effect of drying temperature on PAE curing

PAE resins are thermosetting and the drying conditions on the paper machine are critical to wet strength development. Fig. 9-11 illustrates the effect of curing temperature on the rate and magnitude of wet strength development. The practical implications are that the drying program on a paper machine has a profound effect on the curing rate and final wet strength level attained. This means that a machine producing a given grade to the same final moisture content may nevertheless obtain different wet strength results if dryer section drying times and temperatures differ between grade runs.

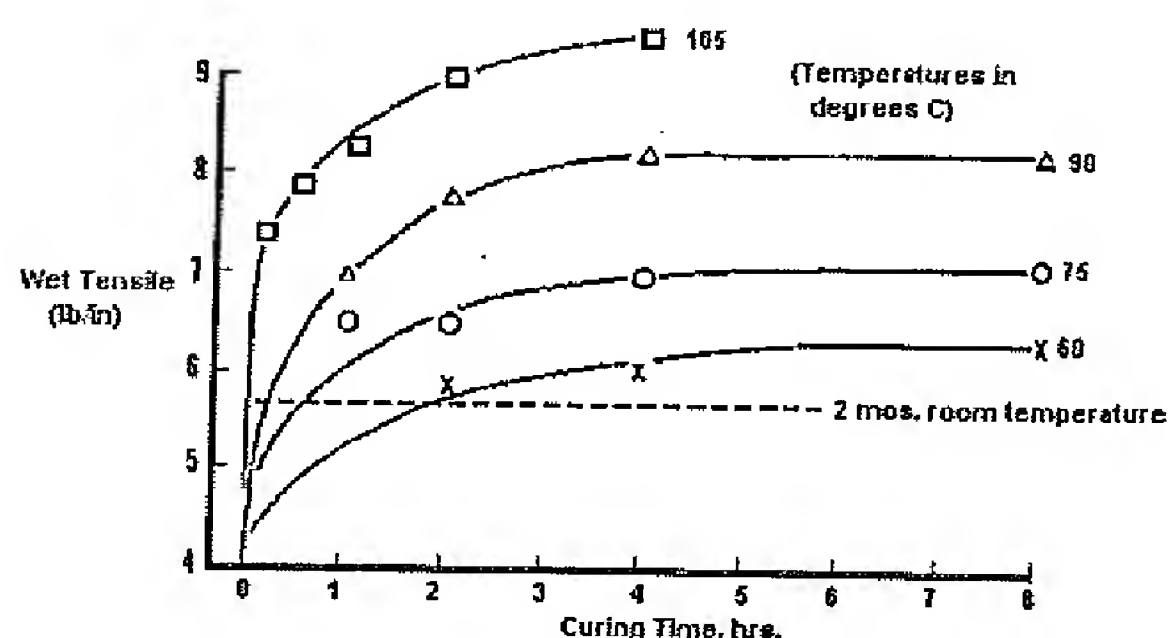


Figure 9-11. Effect of drying time and drying temperature on the development of wet strength

13. Summary

It is clear from the preceding discussion that wet strength wet end chemistry is complex and that the attainment of high wet strength levels and efficient resin utilization requires close attention to technical details. As is the case with cationic dry strength resins, rapid and efficient polymer retention (adsorption) is very important and system conditions and chemistry should be established to promote this goal. With wet strength resins, however, high retention does not always mean good wet strength performance because curing reactions must also occur.

14. References

- [1] Espy, H. "Wet strength resins." Chapter IV in *Pulp and Paper Manufacture*, Volume 6: Stock Preparation. Editors R. W. Hagemeyer and D. W. Manson, Joint Textbook Committee of the Paper Industry, 1992, pp. 65-85.
- [2] Dunlop-Jones, N. "Wet strength chemistry." Chapter 6 in *Paper Chemistry*. Edited by J. C. Roberts, Chapman and Hall, New York, 1991, pp. 76-96.
- [3] Cates, R. "Wet strength resins." Chapter 9 in *Chemical Processing Aids in Papermaking: A Practical Guide*. Edited by K. Hipolit, TAPPI PRESS, Atlanta, 1992, pp. 129-148.
- [4] Eklund, D. and Lindstrom, T. "Wet Strength." Chapter IV in *Paper Chemistry: An Introduction*. DT Paper Science Publications, Grankulla, Finland, 1991, pp. 89-105.
- [5] Pahl, B. L. and Espy, H. H. "Advanced topics in papermaking with alkaline-curing polyamide wet strength resins." In *Notes from 1987 Advanced Topics in Wet End Chemistry Seminar*, October, 14-16, 1987, Memphis, TN. TAPPI PRESS, 1987, pp. 77-82.

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Filler: Paper

1. Intro

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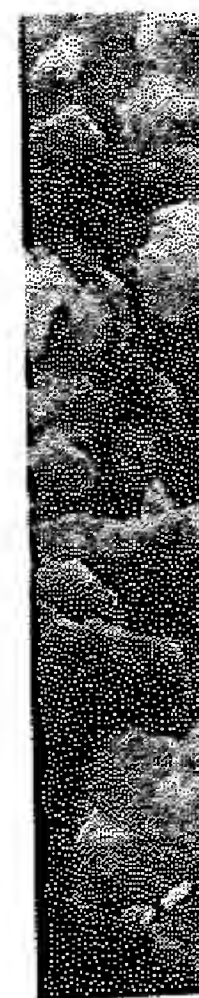


Figure 1
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